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# Diffusion Coefficients of Sodium Fluoride in Aqueous Solutions at 298.15 K and 310.15 K

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## Abstract

Mutual diffusion coefficients (interdiffusion coefficients) have been measured for sodium fluoride in water at 298.15 K and 310.15 K at concentrations between 0.003 mol dm<sup>-3</sup> and 0.05 mol dm<sup>-3</sup>. The diffusion coefficients were measured using a conductimetric cell. The experimental mutual diffusion coefficients are discussed on the basis of the Onsager-Fuoss model. The limiting molar conductivity of the fluoride ion in these solutions at 310.15 K has been estimated using these results.

**Keywords:** Diffusion, electrolytes, solutions, sodium fluoride, transport properties.

## 1. Introduction

The knowledge of electrolytes diffusion data is important for essential reasons, helping to understand the nature of aqueous electrolyte structure, and for its practical application in many everyday technical fields, for instance, dental corrosion. However, the magnitude and behaviour of these transport properties for electrolytic systems in the oral cavity are poorly known, even though this is a prerequisite to obtain adequate understanding and solution of these corrosion problems.

For some time, the research interest of our group has been focused on dental restoration and therefore in obtaining data (not available in the literature) of the transport properties for ionic systems involved in the dental damage processes in the oral cavity.<sup>1-3</sup> In fact, since oral restoration involves various dental metallic alloys, and the oral cavity is a wet environment, those systems provide favourable conditions for corrosion. This phenomenon has been minimized by the use of fluoride compounds, under different systemic and topical forms, which prevent an anti-caries action.<sup>4,5</sup> This has provided the impetus for the present study of the diffusion of these fluoride ions in aqueous solutions.

As far as the authors know, no data on mutual diffusion coefficients of sodium fluoride have been published at physiological temperature.<sup>6</sup> Consequently, in the present study mutual diffusion coefficients,  $D$ , (interdiffusion coefficients) are reported at this temperature, together with those at 298.15 K, for aqueous solutions of sodium fluoride in the concentration range from 0.003 to 0.05 mol dm<sup>-3</sup>, by using an open-ended conductimetric capillary cell.<sup>7-29</sup> These results are discussed on the basis of the Onsager-Fuoss mode.<sup>30-33</sup> At this stage, no attempt is made to split mutual diffusion data into their individual contributions since for practical purposes, such as the chemistry in the oral cavity, is the global value what is required.

## 2. Experimental Section

### 2.1. Materials

Sodium Fluoride (J. T. Baker, pro analysis > 99%) was used without further purification.

The solutions for the diffusion measurements were prepared in calibrated volumetric flasks using bi-distilled water. The solutions were freshly prepared and de-aerated for about 30 min before each set of runs.

## 2. 2. Diffusion Measurements

An open-ended capillary cell, which has been used to obtain mutual diffusion coefficients for a wide variety of electrolytes,<sup>7–9</sup> is described in great detail in previous papers.<sup>7–29</sup> and so only some relevant points concerning this method on the experimental determination of binary diffusion coefficients,  $D$  are described.

Basically, this consists of two vertical capillaries, each closed at one end by a platinum electrode, and positioned one above the other with the open ends separated by a distance of about 14 mm. The upper and lower tubes, initially filled with solutions of concentrations  $0.75 c$  and  $1.25 c$ , respectively, are surrounded with a solution of molar concentration,  $c$  (defined in mol dm<sup>-3</sup>). This ambient solution is contained in a glass tank (200 × 140 × 60) mm immersed in a thermostat bath at 298.15 K. Perspex sheets divide the tank internally and a glass stirrer creates a slow lateral flow of ambient solution across the open ends of the capillaries. Experimental conditions are such that the concentration at each of the open ends is equal to the ambient solution value  $c$ , that is, the physical length of the capillary tube coincides with the diffusion path. This means that the required boundary conditions described in the literature<sup>8,9</sup> to solve Fick's second law of diffusion are applicable. Therefore, the so-called  $\Delta l$  effect<sup>8,9</sup> is reduced to negligible proportions. In our manually operated apparatus, diffusion is followed by measuring the ratio  $w = R_t/R_b$  of resistances  $R_t$  and  $R_b$  of the upper and lower tubes by an alternating current transformer bridge. In our automatic apparatus,  $w$  is measured by a Solartron digital voltmeter (DVM) 7061 with 6 1/2 digits. A power source (Bradley Electronic Model 232) supplies a 30 V sinusoidal signal at 4 kHz (stable to within 0.1 mV) to a potential divider that applies a 250 mV signal to the platinum electrodes in the top and bottom capillaries. By measuring the voltages  $V'$  and  $V''$  from top and bottom electrodes to a central electrode at ground potential in a fraction of a second, the DVM calculates  $w$ .

In order to measure the differential diffusion coefficient  $D$  at a given concentration  $c$ , the bulk solution of concentration  $c$  is prepared by mixing 1 L of "top" solution with 1 L of "bottom" solution, measured accurately. The glass tank and the two capillaries are filled with  $c$  solution, immersed in the thermostat, and allowed to come to thermal equilibrium. The resistance ratio  $w = w_\infty$  measured under these conditions (with solutions in both capillaries at concentration  $c$ ) accurately gives the quantity  $\tau_\infty = 10^4 / (1 + w_\infty)$ .

The capillaries are filled with the "top" and "bottom" solutions, which are then allowed to diffuse into the "bulk" solution. Resistance ratio readings are taken at various recorded times, beginning 1000 min after the start of the experiment, to determine the quantity  $\tau = 10^4 / (1 + w)$  as  $\tau$  approaches  $\tau_\infty$ .

Considering the quantities  $Y_t$  and  $Y_\infty$  defined by the equations

$$Y_t = (W - 1) / (W + 1) \quad (1)$$

$$Y_\infty = (w_\infty - 1) / (w_\infty + 1) \quad (2)$$

and  $t > 1000$  min, it is possible to evaluate the diffusion coefficient by using the corresponding slope of the equation (3)

$$\ln(Y_t - Y_\infty) = \text{constant} - \lambda t \quad (3)$$

$$\lambda = (\pi^2 D) / (4 a^2) \quad (4)$$

Therefore, plotting the experimental results  $\ln(Y_t - Y_\infty)$  as a function of time, and using an adequate programme of successively interactions coupled with the minimum square deviations method, a straight line equation is obtained, and the corresponding slope is directly proportional to the diffusion coefficient eq (4).

## 3. Results and Discussion

Mutual diffusion coefficients,  $D$ , of sodium fluoride in aqueous solutions at 298.15 K and 310.15 K are shown in Table 1, where  $D$  is the mean value of, at least, three independent measurements. The standard deviations of the means are shown in Table 1. Previous papers reporting data obtained with this conductimetric cell support our view that the inaccuracy of our results should not be much larger than the imprecision. That is, we believe that our uncertainty is not much larger than (1 to 3) %.

For the purposes of this study, it was not necessary to extend the limits in concentration beyond those indicated in Table 1.

A linear dependence on the concentration  $c$  has been found

$$D = a_0 + a_1 c \quad (5)$$

where the coefficients  $a_0$  and  $a_1$ , are adjustable parameters obtained by fitting the experimental data. Table 2 shows the coefficients  $a_0$  and  $a_1$  of eq 5. These may be used to calculate values of diffusion coefficients at specified concentrations within the range of the experimental data shown in Table 1. The goodness of the fit (obtained with a confidence interval of 98%) can be assessed by the excellent correlation coefficients,  $R^2$ , and the low standard deviation (< 1%).

To understand the transport process of this electrolyte in aqueous solutions, as a first approach the experimental mutual diffusion coefficients at 298.15 K were compared with those estimated by using Onsager-Fuoss equation suitable for dilute solutions [eq 6 (Table 3)]

$$D = \bar{M} \left( \frac{|z_1| + |z_2|}{|z_1 z_2|} \right) \frac{RT}{c} \left( 1 + c \frac{\partial \ln \gamma_{\pm}}{\partial c} \right) \quad (6)$$

**Table 1:** Diffusion coefficients,  $D$  of NaF in aqueous solutions at various concentrations,  $c$ , and the standard deviations of the means,  $S_D$ , at 298.15 K and 310.15 K.

$c/\text{mol dm}^{-3}$	$T = 298.15 \text{ K}$			$T = 310.15 \text{ K}$	
	$D/10^{-9} \text{ m}^2 \text{ s}^{-1 \text{ a}}$	$S_D/10^{-9} \text{ m}^2 \text{ s}^{-1 \text{ b}}$	$\Delta D/D_{\text{Lit}}^{\text{c}}$	$D/10^{-9} \text{ m}^2 \text{ s}^{-1 \text{ a}}$	$S_D/10^{-9} \text{ m}^2 \text{ s}^{-1 \text{ b}}$
0.000	1.370 <sup>d</sup>	–	–2.2 <sup>e</sup>	2.038 <sup>d</sup>	–
0.003	1.368	0.015	1.0	2.017	0.010
0.005	1.365	0.020	1.1	2.009	0.029
0.008	1.364	0.019	1.1	2.005	0.017
0.010	1.353	0.015	1.0	2.003	0.010
0.030	1.328	0.020	0.6	1.899	0.009
0.050	1.300	0.005	–0.8	1.804	0.005

<sup>a</sup> $D$  is the mean diffusion coefficient for 3 experiments <sup>b</sup> $S_D$  is the standard deviation of that mean. <sup>c</sup> $\Delta D/D_{\text{Lit}}$  represent the relative deviations between our diffusion coefficients,  $D$  (Table 1), and experimental  $D$  values obtained from Taylor technique,<sup>6</sup> respectively. <sup>d</sup> $D$  extrapolated using our data (Table 1). <sup>e</sup>Relative deviations between  $D$  extrapolated using our data and the Nernst value (eq 10) using data from ref 39.

**Table 2:** Fitting coefficients ( $a_0$  and  $a_1$ ) of the linear dependence  $[D/(\text{m}^2 \text{ s}^{-1}) = a_0 + a_1 (c/\text{mol dm}^{-3})]$  to the mutual differential diffusion coefficients for sodium fluoride in aqueous solutions at 298.15 K and 310.15 K<sup>a</sup>

$T/\text{K}$	$a_0/10^9 \text{ m}^2 \text{ s}^{-1}$	$a_1/10^9 \text{ m}^2 \text{ s}^{-1}$	$R^2 \text{ a}$
298.15	1.372	–1.449	0.991
310.15	2.038	–4.647	0.993

<sup>a</sup> See page 6.

where  $D$  is the mutual diffusion coefficient of the electrolyte in  $\text{m}^2 \text{ s}^{-1}$ ,  $R$  is the gas constant in  $\text{J mol}^{-1} \text{ K}^{-1}$ ,  $T$  is the absolute temperature,  $z_1$  and  $z_2$  are the algebraic valences of a cation and of an anion, respectively, and the last term in parenthesis is the activity factor, with  $\gamma_{\pm}$  being the mean molar activity coefficient,  $c$  the concentration in  $\text{mol m}^{-3}$ , and  $\bar{M}$ , in  $\text{mol}^2 \text{ s m}^{-3} \text{ kg}^{-1}$ , given by

$$\bar{M} = \frac{1}{N_A^2 e_0^2} \left( \frac{\lambda_1^0 \lambda_2^0}{\nu_2 |z_2| \lambda_1^0 + \nu_1 |z_1| \lambda_2^0} \right) c + \Delta \bar{M}' + \Delta \bar{M}'' \quad (7)$$

In eq 3, the first- and second-order electrophoretic terms, are given by

$$\Delta \bar{M}' = -\frac{c}{N_A} \frac{(|z_2| \lambda_1^0 - |z_1| \lambda_2^0)^2}{(|z_1| \nu_1 \lambda_2^0 + |z_2| \nu_2 \lambda_1^0)^2} \frac{\nu_1 \nu_2}{\nu_1 + \nu_2} \frac{\kappa}{6\pi \eta_0 (1 + \kappa a)} \quad (8)$$

$$\Delta \bar{M}'' = \frac{(\nu_1 |z_2| \lambda_1^0 + \nu_2 |z_1| \lambda_2^0)^2}{(\nu_1 |z_1| \lambda_2^0 + \nu_2 |z_2| \lambda_1^0)^2} \frac{1}{(\nu_1 + \nu_2)^2} \frac{1}{N_A^2} \frac{\kappa^4 \phi(\kappa a)}{48\pi^2 \eta_0} \quad (9)$$

where  $\eta_0$  is the viscosity of the water in  $\text{N s m}^{-2}$ ,  $N_A$  is the Avogadro's constant,  $e_0$  is the proton charge in coulombs,  $\nu_1$  and  $\nu_2$  are the stoichiometric coefficients,  $\lambda_1^0$  and  $\lambda_2^0$  are the limiting molar conductivities of the cation and anion, respectively, in  $\Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$ ,  $\kappa$  is the “reciprocal average radius of ionic atmosphere” in  $\text{m}^{-1}$  (see e.g.,<sup>34</sup>),  $a$  is the mean distance of closest approach of ions in m,  $\phi(\kappa a) = |e^{2\kappa a} E_1(2\kappa a)/(1 + \kappa a)|$  has been tabulated by Harned and Owen,<sup>34</sup> and the other letters represent well-known quantities.<sup>34</sup> In this equation, phenomena such as hydrolysis,<sup>35,36</sup> complexation and/or ion association,<sup>37</sup> are not taken into consideration. There is no direct method for measuring the ion size parameter  $a$ , “mean distance of closest approach” from the Debye-Hückel theory, but it may be estimated from different methods by using experimental and theoretical approaches for sodium salts (e.g., from mean ionic activity coefficients and diffusion coefficients, and ab initio calculations and molecular mechanic studies (MM2)).<sup>38</sup>

Concerning the values of parameter  $a$  obtained by adjustment of Onsager–Fuoss equation to the experimental data of diffusion coefficients, we see that, in general, we should note that calculations based on eq 2 are not greatly affected by the choice of the ion size parameter  $a$ , within the limits indicated (Table 3). For example, comparing the calculated diffusion coefficients of sodium fluoride,  $D_{OF}$  (Table 3), using the three different values of this parameter  $a$ , with the related experimental values at 298.15 K (Table 1), a reasonable agreement is observed between the experimental data and this model (deviations  $\leq 3\%$ ). The deviation between the limiting  $D^0$  value calculated by extrapolating experimental data to  $c \rightarrow 0$  (Table 2) and the Nernst value (Table 3) is also acceptable (2.2%). The decrease of the diffusion coefficient, when the concentration increases, may be interpreted, among other factors, on the basis of species resulting from the eventual formation of ion pairs, increasing these phenomena with concentration. In relation to the effect of temperature on diffusion, an increase in the experimental  $D$

**Table 3:** Diffusion coefficients of sodium fluoride calculated from Onsager-Fuoss theory,  $D_{OF}$ , at 298.15 K.<sup>30–32</sup>

$c/\text{mol dm}^{-3}$	$D'_{OF}/10^{-9} \text{ m}^2 \text{ s}^{-1}$	$\Delta D/D'_{OF} / \%$	$D''_{OF}/10^{-9} \text{ m}^2 \text{ s}^{-1}$	$\Delta D/D''_{OF} / \%$	$D'''_{OF}/10^{-9} \text{ m}^2 \text{ s}^{-1}$	$\Delta D/D'''_{OF} / \%$
	a)	b)	c)	b)	d)	b)
0.000	1.401	-2.5 <sup>e)</sup>	1.401	-2.5 <sup>e)</sup>	1.401	-2.5 <sup>e)</sup>
0.003	1.367	0.07	1.365	0.4	1.364	0.3
0.005	1.360	0.4	1.361	-0.1	1.363	-0.1
0.008	1.352	0.9	1.351	1.0	1.352	0.9
0.010	1.346	0.5	1.350	0.2	1.354	-0.1
0.030	1.329	-0.1	1.335	-0.5	1.339	1.0
0.050	1.310	-0.8	1.326	-2.0	1.340	-2.9

Notes: a)  $a = 2.2 \times 10^{-10}$  m obtained from the sum of the ionic radii (obtained from diffraction methods).<sup>40</sup> b)  $\Delta D/D'_{OF}$ ,  $\Delta D/D''_{OF}$  and  $\Delta D/D'''_{OF}$  represent the relative deviations between  $D$  (Table 1) and  $D'_{OF}$ ,  $D''_{OF}$  and  $D'''_{OF}$  values, respectively. c)  $a = 4.6 \times 10^{-10}$  m estimated using MM2.<sup>41</sup> d)  $a = 7.1 \times 10^{-10}$  m estimated using MM2.<sup>41</sup> e) Relative deviations between  $D$  extrapolated (Table 1) and the Nernst value (eq 10).

values was found at all sodium fluoride concentrations. Also, the decrease of the diffusion coefficient was obtained when the concentration increases. However, given the absence of the values of parameters for estimations of  $D_{OF}$ , only the diffusion coefficient of sodium fluoride at infinitesimal concentration and the equivalent conductance of the fluoride ion were estimated.

From the following equation for analysis of the data, shown in Table 2, we estimated the diffusion coefficient of sodium fluoride at infinitesimal concentration as  $D^0 = 1.372 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and  $D^0 = 2.038 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  at 298.15 K and 310.15 K, respectively. To estimate  $\lambda_{F^-}^0$  at 298.5 K and 310.15 K, we may assume that the above  $D^0$  value coincides with the Nernst value<sup>26</sup> from

$$D^0 = \frac{RT}{F^2} \frac{|Z_{\text{Na}^+}| + |Z_{\text{F}^-}|}{|Z_{\text{Na}^+} Z_{\text{F}^-}|} \frac{\lambda_{\text{Na}^+}^0 \lambda_{\text{F}^-}^0}{\lambda_{\text{Na}^+}^0 |Z_{\text{F}^-}| + \lambda_{\text{F}^-}^0 |Z_{\text{Na}^+}|} \quad (10)$$

where  $Z_{\text{Na}^+}$  and  $Z_{\text{F}^-}$  represent the algebraic valences of a cation and of an anion, respectively.  $\lambda_{\text{Na}^+}^0$  is the molar conductance of  $\text{Na}^+$  at infinitesimal concentration, estimated at 310.15 K by using a polynomial equation fitted to experimental data from reference 39 (that is,  $\lambda_{\text{Na}^+}^0 = 59.0 \times 10^{-4} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$ ). At 298.15 K, the authors used the value found in this reference (that is,  $\lambda_{\text{Na}^+}^0 = 50.10 \times 10^{-4} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$ ). Therefore, from eq 6, we have  $\lambda_{\text{F}^-}^0 = 53.30 \times 10^{-4} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$  and  $\lambda_{\text{F}^-}^0 = 98.10 \times 10^{-4} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$  at 298.15 K and 310.15 K, respectively. The deviation between the  $\lambda_{\text{F}^-}^0$  value calculated by this method at 298.15 K and the value found in the literature is also acceptable (3%).

## 4. Conclusions

In conclusion, we have measured mutual diffusion coefficients (interdiffusion coefficients) for sodium fluoride in water at 298.15 K and 310.15 K at concentrations

between 0.003 mol dm<sup>-3</sup> and 0.05 mol dm<sup>-3</sup>. These diffusion coefficients have been measured having in mind a better understanding of the structure of these systems.

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## Povzetek

Z merjenjem električne prevodnosti v kapilarni celici smo določili difuzijski koeficient natrijevega fluorida v vodi pri 298.15 in 310.15 K v koncentracijskem območju med 0.003 in 0.05 mol dm<sup>-3</sup>. Eksperimentalne vrednosti smo obravnavali z Onsager-Fuossom modelom, s pomočjo katerega smo določili tudi limitno vrednost molske prevodnosti fluoridnega iona v vodi pri 310.15 K.